EXTRACTION OF NAPHTHENIC ACID FROM INDONESIAN CRUDE OILS BY METHANOL-AMMONIUM SOLUTION

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ABSTRACT

Indonesia's crude oil which has a total acid number (TAN) with a concentration more than 0.5 mg KOH/g are often found. The presence of naphtenic acid tends to increase the value of TAN. The existence of naphthenic acid needs to be reduced to avoid problems in the petroleum refining process because it will cause problems of corrosion, foaming, etc. On the other hand, naphthenic acid may have a value-added as an emulsifier, antiseptics timber, preservatives, and so on. This study extracted naphthenic acid from some Indonesian crude oils which have relatively high TAN value oil with the code A, B and C. Extraction of naphthenic acid from crude B shows quite high results of that is equal to 65.47% with a purity level of 96.6%

Keywords: *Naphthenic acid, Extraction, Methanol-Ammonium Solution*

I. INTRODUCTION

There are quite a lot of Indonesian crude oils that have high total acid number (TAN). Crude oil is defined as acid crude oil if the value of TAN is above 0.5 mg KOH / gram. The presence of naphthenic acid in crude oil may increase the total acid number. Naphthenic acids are classified as carboxylic acids which generally have a structure of $R(CH_2)nCOOH$, where R is cycloaliphatic structure (Shi *et al.*, 2008.) and n is a number between 6-40 (Shalaby, 2005).

The presence of relatively high level of naphthenic acids in oil can cause problems in petroleum refining process such as problem of corrosion, foaming and also catalyst deactivation (Wang *et al*., 2006.). Some crudes contain sufficient quantities of organic acid, generally naphthenic acids, to cause severe problems in units operating above 230°C (Shalaby, 2005). Naphtenic acids corrosion often occurs in the same places as high temperature sulfur attack such as heater tube outlet, transfer lines, column flush zone and pumps (Shalaby, 2005). On the other hand, naphthenic acids can be used as raw materials for industries such as a timber antiseptic, a paint drying reagent, an additives in petroleum, etc. (Shi *et al*., 2008), whereas naphthenate salts can be used as catalysts, preservatives, corrosion inhibitors, emulsifiers and dispersants (Wang ***et.al***., 2006). Therefore, separation and purification of naphthenic acids in crude oils are expected. Separation of naphthenic acid from crude oil said to be efficient if it has TAN of greater than 0.2 mg KOH / g (Danzik *et al.,* 1987).

Several attempts have been made to reduce naphthenic acid in crude oil problems, among others, with an ionic liquid (Shi *et.al*, 2008), ethylene glycol-ammonium solution (Wang *et al*., 2006), QAE Sephadex A-25 (Mediaas et. al, 2003; Mohammed, 2009).

This paper was written to report the results of the separation naphthenic acid analysis of some Indonesian oil using methanol and extraction with ammonium solution. This analysis was a preliminary study to develop further research for reducing acid content in crude oil.

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II. EXPERIMENTAL

A. Materials

All chemicals used, such as methanol, toluene and ammonium hydroxide, a solvent (mixture of toluene, 2-propanol and water) are not subjected to further purification. The crude oil was from some fields in Indonesia. The properties of crude oil are listed in Table 1. The crude oil used in the study had a TAN of above 0.2 mg KOH/gr.

B. Extraction Process

Extraction process is done by mixing solvent and crude oil in a separating funnel of 500 ml and then shaken for five minutes. There after, the separating funnel is kept for sixteen hours at room temperature. Two layers are formed in the funnel. Water-soluble phase, the bottom layer, is removed through the spout. Then the top layer which is the crude oil is extracted with solvent again. The extraction process is carried out four times.

The layer of water that has been obtained from the extraction and centrifuge is inserted into the rotary evaporator with rotation at 30 per minute and temperature of 60-80 °C for 1-2 hours. After evaporation with a rotary evaporator there will be a solution of ammonia in the container and naphthenic acid stick to the flask wall.

C. Determination of TAN, Acid Removal and Purity of Naphthenic acids

Determination of TAN in crude oil is based on standard method ASTM D 664 and the formula is calculated using equation 1.

Acid number, mg KOH/g = (A-B) x Mx56.1/W..(1)

where:

A : volume of KOH solution used to titrate sample, ml

B : volume corresponding to A for blank titration, ml

N : concentration of KOH solution, mol/L

W : sample mass, g

Determination of the percentage of acid-removal using the equation 2

$$\%\ \text{aci dremoval} = \frac{\text{TAN}_{\text{after}}}{\text{TAN}_{\text{before}}} \text{ x } 100\% \quad \text{..... (2)}$$

While the equation for determining the purity napthenic acid produced using the equation 3

$$\%\ \text{acid purity} = \frac{\text{TAN}_{\text{before}}}{\text{TAN}_{\text{after}}} \text{ x } 100\% \quad \text{.....(3)}$$

D. Purification

Naphthenic acid in a round flask is dissolved with toluene in rotary evaporator. Toluene solution containing naphthenic acid is washed with distilled water until the color is clear. The solution of toluene will be evaporated by rotary evaporator with 20 to 30 rpm at 70 to 80 ° C for 2 hours. Then flask weighed up to constant weight.

III. RESULT AND DISCUSSION

Separation of naphthenic acid from crude oil was carried out by liquid-liquid extraction method. Extraction of the three samples showed differences in acid removal. Results of the third crude oil extraction for

Table 1
Characteristic of Crude Oil

Characteristic	Crude A	Crude B	Crude C
Spesific Gravity 60/60^{o}F	0.8034	0.7946	0.8859
API Gravity	44.6	46.6	28.2
TAN (mg KOH/gram)	0.2825	0.5216	0.5844
Viscosity (cSt, 40 ^{o}C)	1.036	1.793	4.108
Characteritic Factor K_{uop}	11.5	12.1	11.3

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the separation of crude B, A and C 64.49%, 49.06% and 21:01% respectively. The TAN was measured before and after treatment can be reported in Table 2.

The highest naphthenic acid purity is indicated by the crude A and crude B with purity 96.98% and 96.59% respectively. Both crude A and B has sodium naphthenate. The number of impurities of the two samples is not too much so that the value generated enough good purification. While for the oil sample C, the value obtained is of relatively low purity of 58.26%, although there are no obstacles in the process of sample preparation or treatment there is appearance of compounds that are not soluble in toluene after the process of purification.

Under certain condition, the naphthenic acids present in acidic crude oil will precipitate with Ca^{2+}- ions that are present in the co-produced water and form calcium naphthenate and, to a lesser extent, other metal naphthenates. This precipitation accumulates predominantly in oil/water separators and de-salters, but naphthenates can also be found in tube and pipelines. This will lead to costly shutdown periods in which through cleaning must take place (Havre, 2002).

Addition of acid will keep the pH low and thereby avoid naphthenate formation. However, such addition is costly, it will increase corrosion problems and and it is environmentaly unfavourable (Havre, 2002)

In refineries, the problem of corrosion caused by naphthenic acid may arise if the stream was in the range 200°C to 420°C. The rate of corrosion caused by naphthenic acid of low-alloy steel 1.25Cr0.5Mo was 0.5 -1.75 mm / year for the TAN value of between 5-6 at a temperature of 274°C (Wang *et al.*, 2011).

Reduction of naphthenic acids in crude oil not only will reduce corrosion problems in the refinery but also reduce the production costs, maintenance costs and environmental impacts.

Table 2
TAN value and Percentage of Acid-Removal

Crude	TAN (mg KOH/g)		Acid-Removal (%)
	before	after	
Crude A	0,2825	0,1386	49.06
Crude B	0,5216	0,3364	64.49
Crude C	0,5844	0,1228	21.01

Table 3
Purity of Naphthenic acids (Na's)

Crude	Mass Na's (gr)		Purity
	before	after	(%)
Crude A	0.28	0.2887	96.98
Crude B	0.1732	0.1793	96.59
Crude C	0.1058	0.1816	58,26

IV. CONCLUSION

- The value obtained for the separation of acid in the crude B is the highest value of 64,49%. When purified, the amount of acid content in this sample was 96,59% of the total amount of acid that could be removed from the initial sample.
- Reduction of naphthenic acids in crude oil not only will be reduce corrosion problems in the refinery but also reduce the production costs, maintenance costs and environmental impacts
- Naphthenic acids which are produced can be used as emulsifiers or other agents.

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